SECOND QUARTERLY REPORT

THE REACTIONS PERTAINING TO ZINC-SILVER AND CADMIUM-SILVER BATTERIES

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ABSTRACT

Zn(II) precipitated with KOH was found to be predominantly ZnO. A slight temperature effect under certain conditions has not been verified. Zn(II) precipitated with NH_3 was found to be predominantly $Zn(OH)_2$; as much as 92% of the precipitate was the hydroxide in some cases.

Cd(II) precipitated with KOH was found to be about 50% or more $Cd(OH)_2$. The fairly pronounced temperature effect has not been verified.

AgO decomposes at a detectable rate at temperatures as low as 80°. The rate may be a serious obstacle to heat-sterilization of dry-charged batteries at temperatures above 100°.

OBJECTIVES

The objectives of the contract are three-fold:

(1) The characterization of cadmium and zinc anodic reaction products.

(2) The thermal decomposition of silver oxide and the measurement of the rate of decomposition of AgO and Ag_2O at various temperatures between 110° and 200° C.

(3) The deposition of silver cathode material on zinc anodes.

This report deals with parts of the first two objectives and will be divided into: (A) the investigation of the precipitates of Zn(II) and Cd(II) formed by precipitation with alkaline solutions and (B) thermogravimetric investigations of AgO.

A. PRECIPITATION OF ZINC AND CADMIUM OXIDES

Experimental

Concentrated $Zn(NO_3)_2$, KOH, and ammonia stock solutions were prepared, standardized, and stored as previously described (1). Concentrated $Cd(NO_3)_2$ stock solutions were prepared from J.T. Baker Reagent Grade material; the first stock solution was standardized gravimetrically (2) while subsequent solutions were standardized polarographically (3).

Analysis of the precipitates for tritium was described in the previous report (1). Analysis of supernatants for tritium was discontinued because a satisfactory interpretation of the small differences observed has not been developed.

Precipitates were analyzed for zinc by diluting an aliquot of the re-dissolved precipitate to a convenient volume and determining the concentration of zinc iodometrically (4). More recently, zinc was determined polarographically (5) by diluting 50-λ aliquots of the redissolved precipitate to 25 ml in an NH_3-NH_4Cl supporting electrolyte and comparing the results with a predetermined calibration curve. Precipitates were analyzed for cadmium polarographically in a similar fashion.

Several groups of experiments were performed to determine the relative amounts of hydroxides in the precipitates formed.

1. Precipitation of Zn(II) and Cd(II) with equivalent KOH without environmental control. Each experiment consisted of three or four precipitations from tritiated solutions and one precipitation from an identical, inactive solution. Sufficient stock, tritiated water (H_2^3O) was added to the salt solutions to provide activities of about 6.5×10^3 dpm/λ of stock. Fifty millimoles of Zn(II) or Cd(II) was precipitated by addition of an equivalent amount of base. The solid was separated, washed and, in some cases, dried by drawing air through the material on a sintered-glass filter. (Analysis of the precipitate for the metal ion eliminated the need for drying and weighing.) The solid was dissolved in a slight excess of 6 VF HNO_3 and the solution diluted to exactly 25 ml with water. 50-λ portions of each solution were transferred to counting vials containing 15 ml of scintillator solution for tritium analysis. Where applicable, 50-λ portions were transferred to the polarograph cell.

2. Precipitation of Zn(II) and Cd(II) with equivalent KOH under nitrogen at controlled temperatures. Precipitation was performed in an apparatus described in Figure 1. The container was immersed in a water bath held at a fixed temperature of $25^\circ \pm 0.3^\circ$ or $55^\circ \pm 0.5^\circ$. The required amount of base was placed in the container, N_2 was passed over the surface while the equivalent amount of salt solution was added at a rate such that the temperature was held within the desired limits. Precipitations required about 10 minutes at 55° and about two hours at 25°. The remainder of the experiment was performed as described in 1. above.

3. Precipitation of Zn(II) with NH_3. Experiments were performed as described in 1. above except that NH_3 was added until the pH of the supernatant reached a pre-selected value. When this value was between 7 and 8, losses of Zn(II) indicated that excessive $Zn(NH_3)_4^{2+}$ was formed. Where the pH was between 6 and 6.5, losses were small.

Preliminary experiments showed that Cd(II) could not be completely precipitated with NH_3 at the concentrations involved here.

4. Precipitation of Zn(II) with excess KOH. Experiments were performed as described in 1. above except that sufficient KOH was added to provide final, calculated supernatant concentrations of 1.0 VF, 2.0 VF, and 5.0 VF KOH. No correction was made for zincate formation.

5. Exchange of tritium between water and Zn(II) precipitate. Dried, weighed precipitate was added to a measured quantity of water in a closed container and stirred magnetically. Where the precipitate initially contained tritium, the water was inactive; where the precipitate was inactive initially, tritium was added to the water. At intervals, 50-λ portions of supernatant were taken for analysis. The total volume was corrected for sample removal. At the end of the run, the tritium and Zn(II) content of the precipitate was determined. No attempt was made to control temperature.

Results and Discussion

Any $Zn(OH)_2$ formed should contain an amount of tritium activity which depends on the amount of tritium added, the moles of hydrogen atoms added to the system either as water or as hydroxide, and the amount of $Zn(OH)_2$ precipitated. The "expected" activity is that which should be found if all of the Zn(II) formed the hydroxide; its calculation has been described (1). The ratio of the activity found to that expected should indicate the relative amount of $Zn(OH)_2$ in the precipitate.

Table 1 summarizes the results where equivalent amounts of $Zn(NO_3)_2$ and KOH were mixed. Data from the first two experiments suggest a significant difference in the $Zn(OH)_2$ content at the two different temperatures, although conditions were not controlled carefully. The results shown for the second experiment comprise a combination of data from runs in which conditions were changed within the group. The effects of these changes, if any, are not known.

Results from experiments 3 and 4 seem to contradict those of the first two. The $Zn(OH)_2$ content appears to be independent of the temperature of the precipitation. It must be remembered that, in the second group, Zn(II) solution was added to KOH solution, temperature was carefully controlled throughout the precipitation, and air was excluded from the system. In the first group, KOH was added to the Zn(II) solution and little environmental control was exercised.

The apparent behavior observed in the first group is unexpected. One would anticipate that more $Zn(OH)_2$ would be formed at the low temperature. The second group of results seems more reasonable. The standard deviation for experiment 4 is high, thus the true averages may be even closer than is indicated.

Table 2 shows the results of precipitating Zn(II) with NH_3. Apparently, the material produced is predominantly $Zn(OH)_2$. The percentage of $Zn(OH)_2$ reported may be low, because the amount of Zn(II) used to calculate the expected activity was based on the weight of precipitate rather than on an analysis for Zn(II).

Table 3 summarizes the results of precipitating Cd(II) with KOH. Considerable amounts of $Cd(OH)_2$ are apparently formed. The final washings taken from the precipitates contained a negligible amount of activity which suggests that the activity found in the precipitates was held tightly. Note that the results of the first cadmium experiment are a combination of data from two different types of experiments. However, the large standard deviation shown results from scatter in the controlled-temperature experiments.

The apparent temperature effect is the opposite of what one would expect, i.e., $Cd(OH)_2$ would be expected to be less stable at higher temperatures. This effect must be verified.

Table 4 summarizes the results of a series of experiments in which the supernatant solution contained excess KOH. Temperature and atmosphere were controlled only approximately and relatively few runs were made. It is difficult to show any definite effect although a trend might be postulated. Again, there seems

to be formation of more hydroxide at the higher temperature. There also seems to be some decrease in hydroxide as the excess KOH increases. This is too slight to be significant at this point. The pattern persists that only a small amount of $Zn(OH)_2$ is formed.

The low activity found in the zinc precipitates could be a result of washing out the activity if the exchange between the hydroxide and water is rapid. This effect does not seem too likely in view of the experiments performed with NH_3 as the precipitant. However, the rate of exchange should be known. Several experiments to determine the exchange have been described above. The results are shown in Tables 5 and 6.

The loss in supernatant activity indicated in Table 5 is too small to be considered. However, the gain in activity of the precipitate is significant, particularly when compared with the results of Table 6 where the final precipitate contains about the same activity. The initially inactive precipitate gained activity and the initially active precipitate lost activity while both finally contained about the same activity. From the standpoint of a chemical equilibrium, one would expect the ratio, $A_s/A_p = K$, where A_s is the activity of the supernatant and A_p is the activity of the precipitate. (These are radioactivities rather than chemical activities.) The two values of K which would be calculated from the data thus far differ by about two orders of magnitude. At this point, one can only state that a measurable exchange rate exists.

Conclusions

The experiments reported here tend to confirm that ZnO is the predominant species formed when KOH and $Zn(NO_3)_2$ are mixed. There appears to be no temperature effect when the zinc solution is added to the KOH solution while temperature is controlled and air excluded.

There may be a temperature effect if the KOH solution is added to the zinc solution or if the rate of mixing is changed.

The data suggest some temperature effect if the supernatant is strongly basic in the zinc precipitations and in the precipitation of Cd(II) with equivalent hydroxide. Furthermore, contrary to expectation, the effect would suggest that the hydroxide is stabilized at higher temperatures. These results must be confirmed.

Exchange between the precipitate and water does occur with roughly a third of the exchange occurring in the first few minutes when active $Zn(OH)_2$ is the precipitate. Thus it is possible that scattered results are caused by irreproducible washing procedures.

Proposed Work

Further precipitations of ZnO and $Cd(OH)_2$ will be performed under rigidly controlled conditions of temperature and mixing rate. Rates of exchange of both $Zn(OH)_2$ and $Cd(OH)_2$ will be determined in water and concentrated KOH. Tritiated water will be added to stock KOH in order to determine whether exchange of tritium between water and OH^- prior to precipitation is required. ZnO will be formed electrolytically and the amount of $Zn(OH)_2$ determined.

B. THERMAL DECOMPOSITION OF AgO

Experimental

The method of obtaining thermograms previously described (1) was modified. Temperature was programmed with the F and M Model 240M programmer for a rate of 5°/min. The hangdown tube was lengthened to extend several centimeters below the bottom of the furnace. The thermocouple lead-in was cemented into a cork stopper which was mounted in the bottom of the hangdown tube so that the sensing element was about 3 mm below the sample (See Figure 2). This procedure did not prove satisfactory for constant-temperature work because the thermocouple was too far from the heating element to prevent serious temperature overshoot during initial adjustment. The thermocouple will be

mounted between the tube and the heating element whenever temperature is to be held constant; the system will be calibrated to relate the control temperature to the sample temperature.

One sample was run at 135° for several hours. The thermocouple was suspended inside the hangdown tube beside the sample support wire. The procedure was unsatisfactory because the support wire was attracted to the ceramic thermocouple-shield by static electricity; when they touched, severe recorder chatter resulted. The experiment was terminated because of this noise.

Results and Discussion

Figure 3 shows two thermograms of chemically-prepared AgO, each weighing about 25 mg. The results were normalized so that the total weight-loss is represented as 1.000.

Half of the weight-loss occurred almost exactly half way between the step portions of the curve; this is quite different from results obtained previously. The reason for the difference has not been determined. If the relationship can be made reproducible, a means of determining mixtures of AgO and Ag_2O may be possible.

The curves show that the material begins to lose weight at a significant rate at about 80° and that this rate is becoming important as low as 120°. By 140°, the rate is changing quite rapidly.

Results of the run at 135° are shown in Figure 4. The flat portion at the beginning of the curve represents a heating lag in the system. The steep portion of the curve was caused by a temperature-overshoot of about 10°. Beyond that discontinuity, the temperature remained 135° ± 2°. The decomposition was rapid and virtually linear for about 1.2 hours, then the rate slowed and appeared to approach some asymptotic value. Visible evidence of metallic silver suggests that the decomposition was continuing but at a very much slower rate.

The experiment was discontinued after 3.3 hours. At that point, the weight-loss corresponded to 87% conversion of AgO

to Ag_2O, although some conversion of Ag_2O to Ag had already occurred. These results have yet to be checked.

Conclusions

Detectable decomposition of AgO occurs as low as 80° and may become significant between 100° and 120°. Fairly rapid decomposition to Ag_2O occurs at 135°, the reaction being almost 90% complete in about four hours. These factors must be considered if dry-charged Ag-Zn or Ag-Cd batteries are to be heat-sterilized.

Proposed Work

Constant-temperature thermograms at various temperatures will be determined. The effect of light on the behavior of the decomposition will be investigated.

Table 1

Precipitation of ZnO with KOH

Expt Number	n[1]	Temp (°C)	Zn(II) Recovered (meq)	A expected (dpm x 10^{-6})	A found (dpm x 10^{-4})	% $Zn(OH)_2$	Standard Deviation (%)
1	2	≤55	100[2]	3.9[2]	8.5	2.2	---
2	9	≤25	100[2]	3.9[2]	47.0	12.1	4.7
3	3	25.3 ± 0.3	104[3]	3.76[3]	23.2	6.2	0.3
4	3	55 ± 0.5	101	3.76	23.0	5.0	2.4

(1) Number of runs, each consisting of three or four precipitations, in each experiment.

(2) Zn(II) recovered and expected activity bases on assumed recovery of all zinc in system.

(3) Zn(II) recovered determined by analysis. Expected activity calculated on the basis of 100 meq. Zn(II) recovered.

Table 2

Precipitation of $Zn(OH)_2$ with NH_3

Expt Number	n [1]	Temp (°C)	Zn(II) Recovered (meq)	A expected (dpm x 10^{-6})	A found (dpm x 10^{-6})	% $Zn(OH)_2$	Standard Deviation (%)
1 [2]	1	≤52	48 [3]	2.5 [3]	1.8	72	---
2 [2]	1	<25	67 [3]	3.5 [3]	2.3	67	---
3 [4]	1	<25	92 [3]	4.8 [3]	4.4	92	---
4 [4]	3	<25	100 [5]	5.2 [5]	4.4	86	14.2

[1] Number of runs, each consisting of three precipitations, in each experiment.

[2] pH of supernatant ~ 7-8.

[3] Based on weight of precipitate recovered.

[4] pH of supernatant ~ 6-6.5.

[5] Based on assumption that all Zn(II) recovered.

Table 3

Precipitation of $Cd(OH)_2$ with KOH

Expt Number	n[1]	Temp (°C)	Cd(II) Recovered (meq)	A expected (dpm x 10^{-6})	A found (dpm x 10^{-6})	% $Cd(OH)_2$	Standard Deviation (%)
1[2]	7	25.3 ± 0.3	95.9	3.66	1.76	48.2	6.3
2	3	55 ± 0.5	93.7	3.57	2.33	65.1	2.9

[1] Number of runs, each consisting of three or four precipitations, in each experiment.

[2] Temperature was not carefully controlled in three of the runs.

Table 4

Effect of Final Hydroxide Concentration

Expt Number	(1) n	Temp (°C)	Concentration KOH (VF)	Zn(II) Recovered (meq)	A expected (dpm x 10^{-6})	A found (dpm x 10^{-5})	% $Zn(OH)_2$	Standard Deviation (%)
1[2]	3	≤54	1.0	99	7.22	5.25	7.3	0.7
2[2]	2	≤54	2.0	89	5.78	3.77	6.6	---
3[2]	3	≤50	5.0	50	4.20	1.87	4.5	0.3
4[2]	3	<25	1.0	96	6.99	2.89	4.1	2.4
5	3	<25	2.0	89.4	5.83	1.44	2.5	0.5
6	2	<25	5.0	42.3	3.53	1.34	3.8	---

[1] Number of runs, each consisting of three precipitations, in each experiment.

[2] Recovery based on one analysis in each set of runs.

Table 5

Exchange of Tritium Between Water and "ZnO"
Precipitate formed with KOH

Time (days)	Supernatant Activity (dpm x 10^{-8})	Precipitate Activity (dpm/meq)
0	1.1	0
0.17	1.1	___
1.2	1.1	___
2.2	1.1	___
6	1.1	___
7	1.1	3.6×10^{3}

Table 6

Exchange of Tritium Between Water and "$Zn(OH)_2$"
Precipitate formed with NH_3

Time (days)	Supernatant Activity (dpm x 10^{-6})	Precipitate Activity (dpm/meq)
0	0	3.7×10^4
0[1]	0.55	___
0.17	1.1	___
1.2	1.4	___
2.2	1.4	___
6	1.5	___
7	1.5	3.4×10^3

[1] Sample taken immediately after mixing water with precipitate.

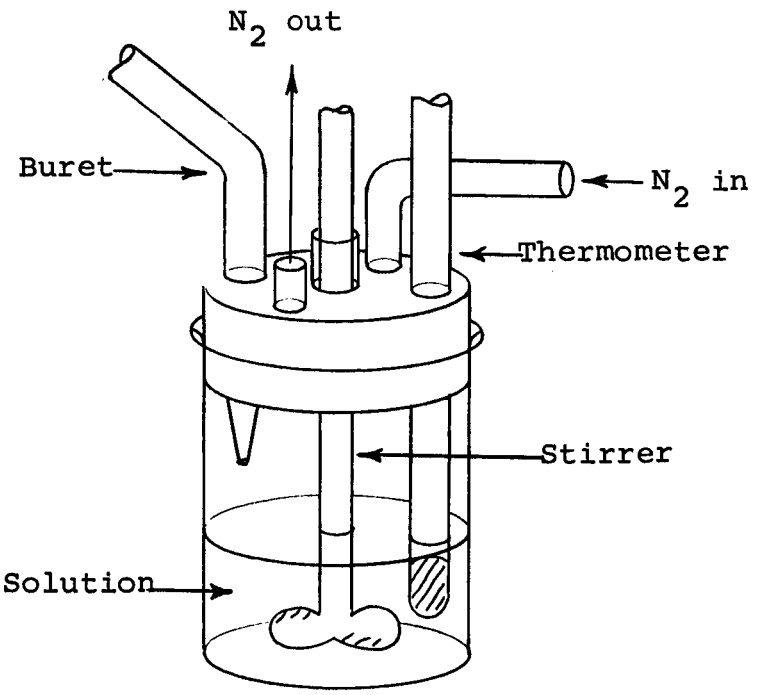

Figure 1. Precipitation Vessel.

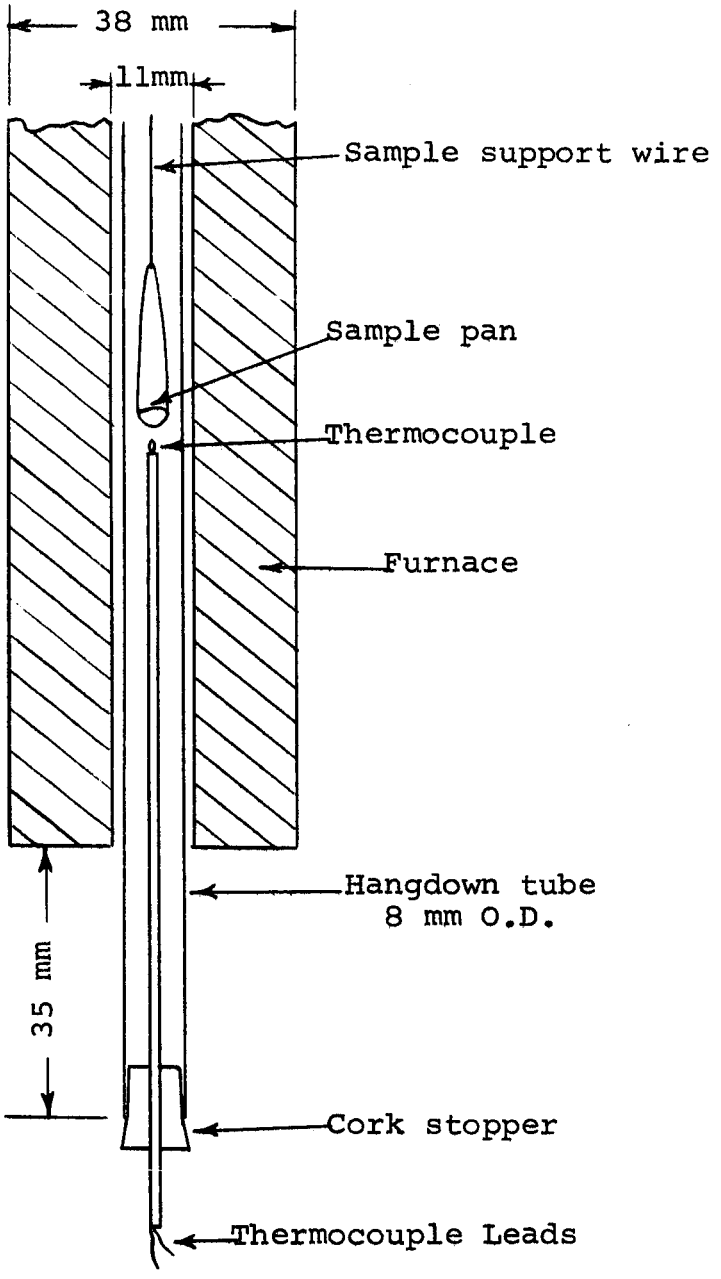

Figure 2. Configuration of Thermogravimetric Heater.

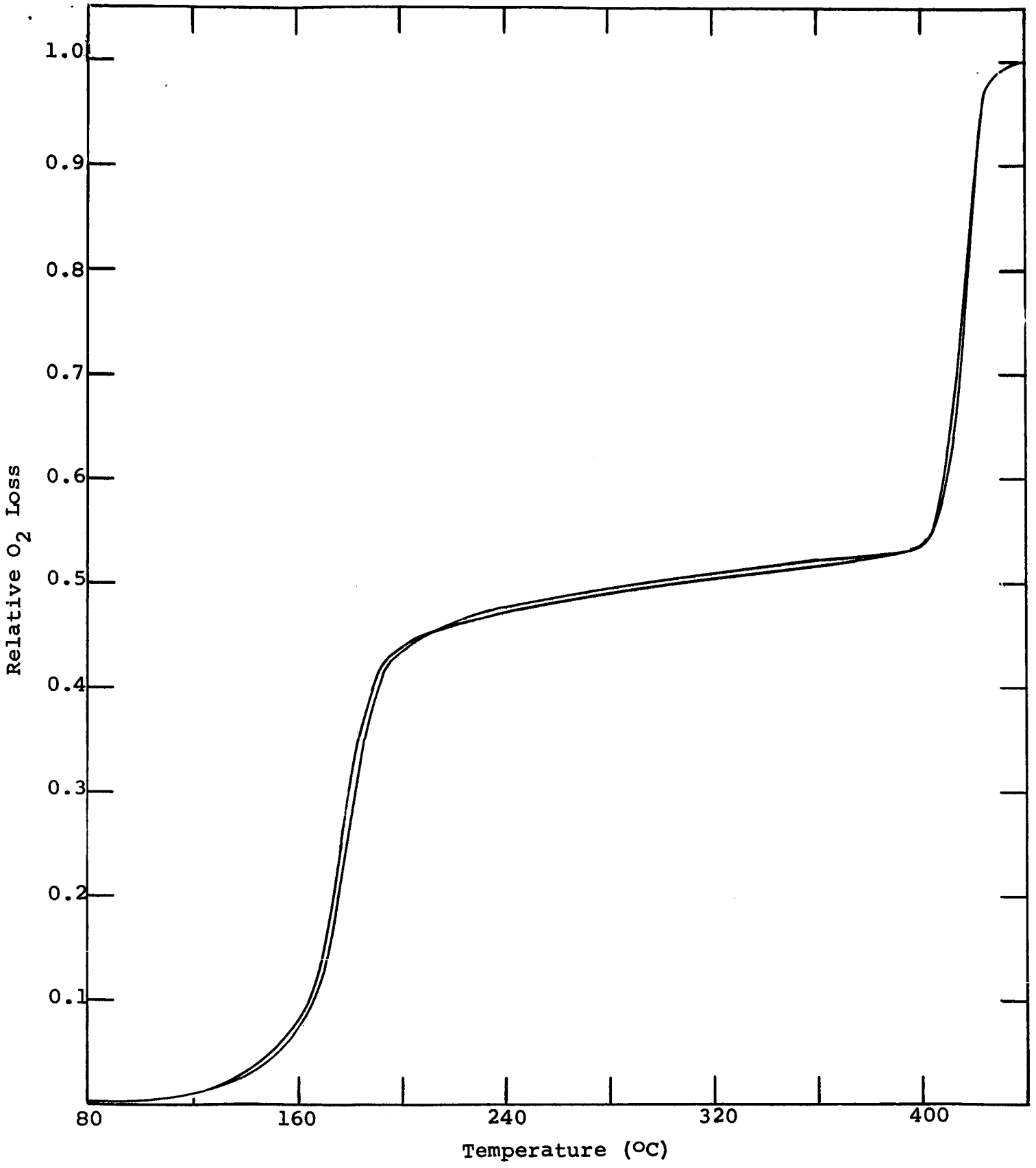

Figure 3. Thermograms of AgO at ΔT Rate of 5°/ Minute

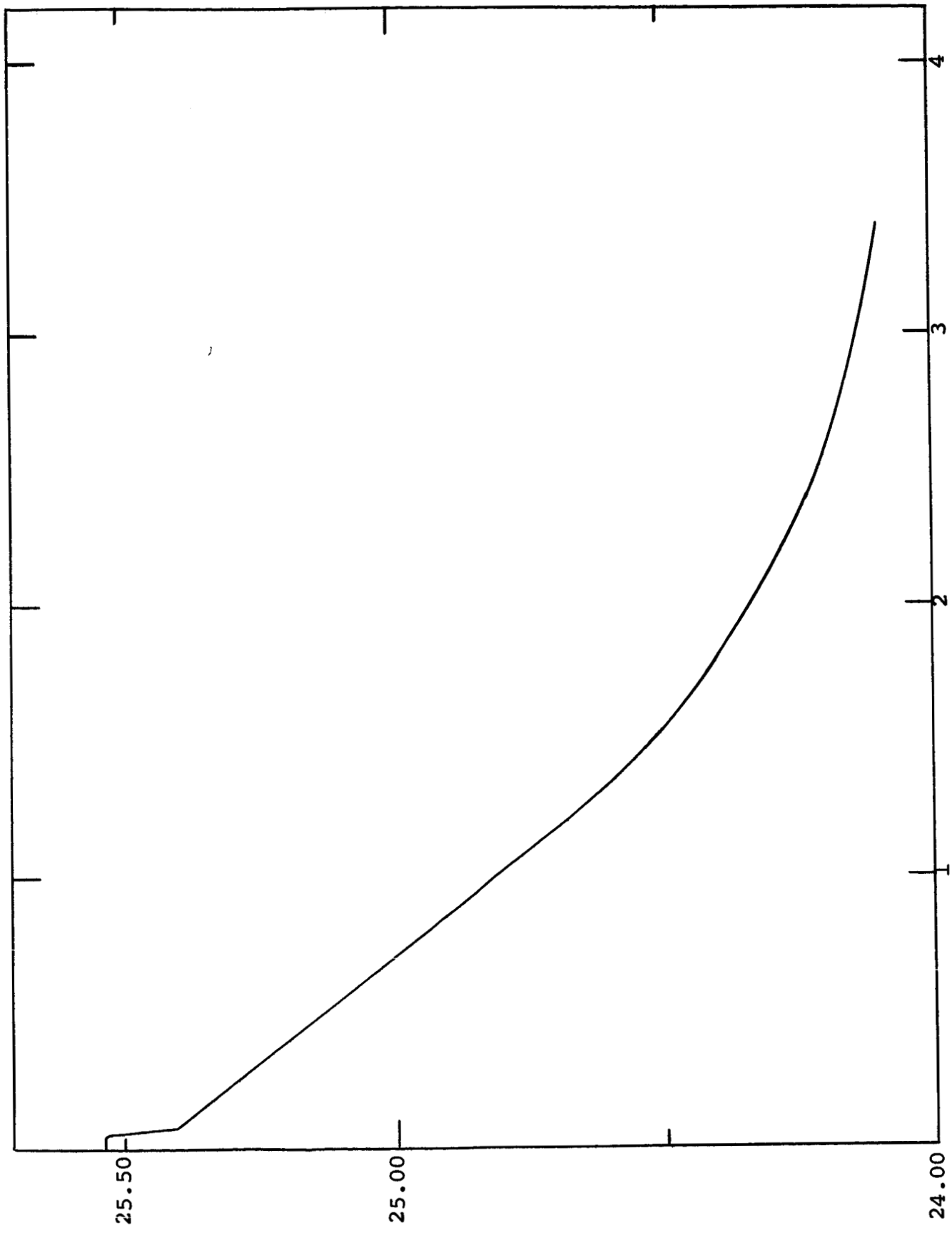

Figure 4. Constant Temperature Thermogram of AgO at 135°.

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